Molecular Simulation of Hydration and Na + Cl- Pair Association in High-Temperature Aqueous Solutions along Sub- and Supercritical Isotherms.

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An extensive molecular-based study of ion-pair formation in near-critical dilute aqueous solutions is performed along three near- (super- and sub-) critical isotherms and from liquid-like to steam-like densities. The study encompasses the determination of the ion-pair association constant via potential of mean force calculations. The main goal is to find answers to some relevant questions regarding the thermodynamic and corresponding microscopic behavior of the ion-pair formation at steam-like densities, where experimental data are either scarce or extremely difficult to obtain accurately. In particular, we address the density dependence of the 'mean hydration numbers' for the ion pair along a near-critical isotherm, the accuracy of the dielectrically screened potential model for ion-pair association, testing the adequacy of the intermolecular model to represent the actual ion-pair behavior in steam, and assessing the hypotheses invoked in current theoretical development on the modeling of ion association in steam-like solutions. Toward that end we make direct contact between simulation, theoretical developments and experiment to aid the interpretation of experimental data and their macroscopic modeling.